PHY 752 Solid State Physics
11-11:50 AM MWF Olin 107

Plan for Lecture 8:

Reading: Chapter 8 in MPM; Electronic Structure

1. **Atom**
2. **Molecule**
3. **Solid**
4. **Linear combination of atomic orbital (LCAO) method**

Course schedule for Spring 2015

(Preliminary schedule -- subject to frequent adjustment.)

	Lecture date	MPM Reading	Topic	Assign.	Due date
1	Mon: 01/12/2015	Chap. 1 & 2	Crystal structures	#1	01/23/2015
2	Wed: 01/14/2015	Chap. 1 & 2	Some group theory	#2	01/23/2015
	Fri: 01/16/2015	No class	NAWH out of town		
	Mon: 01/19/2015	No class	MLK Holiday		
3	Wed: 01/21/2015	Chap. 1 & 2	Some group theory	#3	01/23/2015
4	Fri: 01/23/2015	Chap. 1 & 2	Some more group theory	#4	01/26/2015
5	Mon: 01/26/2015	Chap. 7.3	Some more group theory	#5	01/28/2015
6	Wed: 01/28/2015	Chap. 6	Electronic structure; Free electron gas	#6	01/30/2015
7	Fri: 01/30/2015	Chap. 7	Electronic structure; Model potentials	#7	02/02/2015
8	Mon: 02/02/2015	Chap. 8	Electronic structure; LCAO	#8	02/04/2015

Electronic structure of an atom

For simplicity we will first consider a single electron system; a H-like ion with atomic charge *Ze*

$$H = -\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{4\pi\epsilon_0 r}$$

E_{100}=-13. 60569253 Z² eV
a_0 = 0. 52917721092 Å

$$H\Psi_{nlm}(r,\theta,\phi) = E_{nlm}\Psi_{nlm}(r,\theta,\phi)$$

$$E_{nlm} = -\frac{Z^2e^2}{4\pi\epsilon_0 a_0}\frac{1}{2n^2} \equiv \frac{E_{100}}{n^2} \qquad a_0 \equiv \frac{4\pi\epsilon_0\hbar^2}{me^2}$$

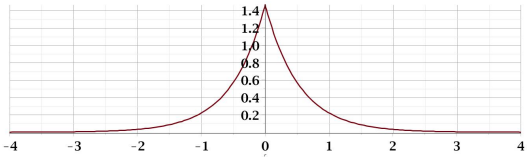
$$\Psi_{100}(r,\theta,\phi) = \sqrt{\frac{Z^3}{\pi a_0^3}}e^{-Zr/a_0} \qquad E_{100} = E_{100}$$

$$\Psi_{200}(r,\theta,\phi) = \sqrt{\frac{Z^3}{32\pi a_0^3}}\left(2 - \frac{Zr}{a_0}\right)e^{-Zr/2a_0} \qquad E_{200} = \frac{E_{100}}{4}$$

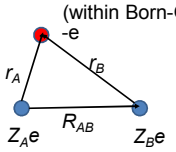
$$\Psi_{210}(r,\theta,\phi) = \sqrt{\frac{Z^3}{32\pi a_0^3}}\frac{Zr}{a_0}e^{-Zr/2a_0}\cos\theta \qquad E_{210} = \frac{E_{100}}{4}$$

$$\Psi_{21\pm1}(r,\theta,\phi) = \mp\sqrt{\frac{Z^3}{64\pi a_0^3}}\frac{Zr}{a_0}e^{-Zr/2a_0}\sin\theta\, e^{\pm i\phi} \qquad E_{21\pm1} = \frac{E_{100}}{4}$$

$$\Psi_{100}(r,\theta,\phi) = \sqrt{\frac{Z^3}{\pi a_0^3}} e^{-Zr/a_0}$$



Electronic structure of H-like molecular ion (within Born-Oppenheimer approximation)



$r_A = |\mathbf{r} - \mathbf{R}_A|$ $\quad r_B = |\mathbf{r} - \mathbf{R}_B|$

$R_{AB} = |\mathbf{R}_B - \mathbf{R}_A|$

$$H = -\frac{\hbar^2}{2m}\nabla^2 - \frac{Z_A e^2}{4\pi\epsilon_0 r_A} - \frac{Z_B e^2}{4\pi\epsilon_0 r_B} + \frac{Z_A Z_B e^2}{4\pi\epsilon_0 R_{AB}}$$

Approximate wavefunction:

$$\Psi(\mathbf{r},\mathbf{R}_A,\mathbf{R}_B) = X_A \Psi_{100}(\mathbf{r}-\mathbf{R}_A) + X_B \Psi_{100}(\mathbf{r}-\mathbf{R}_B)$$

X_A and X_B can be determined variationally by optimizing

$$E = \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle}$$

Electronic structure of H-like molecular ion – continued

Ref. Pauling and Wilson, *Introduction to Quantum Mechanics* (1935) (now published by Dover)

Necessary integrals:

$$\Delta \equiv \int d^3r \Psi_{100}^*(\mathbf{r}-\mathbf{R}_A)\Psi_{100}(\mathbf{r}-\mathbf{R}_B)$$

$$H_{AA} \equiv \int d^3r \Psi_{100}^*(\mathbf{r}-\mathbf{R}_A) H \Psi_{100}(\mathbf{r}-\mathbf{R}_A) = H_{BB}$$

$$H_{AB} \equiv \int d^3r \Psi_{100}^*(\mathbf{r}-\mathbf{R}_A) H \Psi_{100}(\mathbf{r}-\mathbf{R}_B)$$

Generalized eigenvalue problem for energy E in the variational approximation:

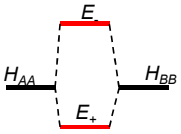
$$\begin{pmatrix} H_{AA} & H_{AB} \\ H_{BA} & H_{BB} \end{pmatrix} \begin{pmatrix} X_A \\ X_B \end{pmatrix} = E \begin{pmatrix} 1 & \Delta \\ \Delta & 1 \end{pmatrix} \begin{pmatrix} X_A \\ X_B \end{pmatrix}$$

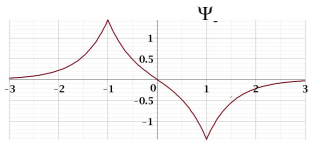
Eigenstates:

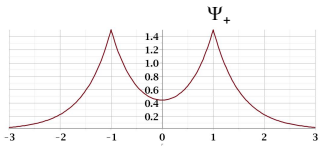
$$\begin{pmatrix} X_A \\ X_B \end{pmatrix}_+ = \frac{1}{\sqrt{2(1+\Delta)}} \begin{pmatrix} 1 \\ 1 \end{pmatrix} \qquad E_+ = \frac{H_{AA} + H_{AB}}{1+\Delta}$$

$$\begin{pmatrix} X_A \\ X_B \end{pmatrix}_- = \frac{1}{\sqrt{2(1-\Delta)}} \begin{pmatrix} 1 \\ -1 \end{pmatrix} \qquad E_+ = \frac{H_{AA} - H_{AB}}{1-\Delta}$$

Electronic structure of H-like molecular ion – continued







Extension of approximate "linear combination of atomic orbital" idea to larger systems

Idealized model Hamiltonian with only nearest neighbor interactions:

$$\begin{pmatrix} \alpha & \beta & \cdots & 0 \\ \beta & \alpha & \cdots & 0 \\ \vdots & \vdots & \cdots & \vdots \\ 0 & 0 & \cdots & \alpha \end{pmatrix} \begin{pmatrix} X_1 \\ X_2 \\ \vdots \\ X_N \end{pmatrix} = E \begin{pmatrix} X_1 \\ X_2 \\ \vdots \\ X_N \end{pmatrix}$$

Extension of approximate "linear combination of atomic orbital" idea to larger systems – some details

$N = 2$ case: $\begin{pmatrix} \alpha & \beta \\ \beta & \alpha \end{pmatrix} \begin{pmatrix} X_1 \\ X_2 \end{pmatrix} = E \begin{pmatrix} X_1 \\ X_2 \end{pmatrix} \quad E = \begin{cases} \alpha + \beta \\ \alpha - \beta \end{cases}$

$N = 4$ case: $\begin{pmatrix} \alpha & \beta & 0 & 0 \\ \beta & \alpha & \beta & 0 \\ 0 & \beta & \alpha & \beta \\ 0 & 0 & \beta & \alpha \end{pmatrix} \begin{pmatrix} X_1 \\ X_2 \\ X_3 \\ X_4 \end{pmatrix} = E \begin{pmatrix} X_1 \\ X_2 \\ X_3 \\ X_4 \end{pmatrix} \quad E = \begin{cases} \alpha + 1.618\beta \\ \alpha + 0.618\beta \\ \alpha - 0.618\beta \\ \alpha - 1.618\beta \end{cases}$

Using ideas from PHY 711, we can show that for N sites, there are N eigenvalues given by

$$E_\nu = \alpha + 2\beta \cos\left(\frac{\pi\nu}{N+1}\right) \quad \text{where} \quad \nu = 1, 2, \ldots N$$

Extension of approximate "linear combination of atomic orbital" idea to larger systems – more details

Consider case where $N \to \infty$:

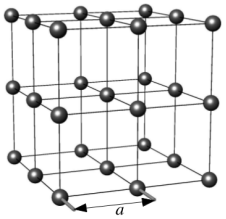
$$\begin{pmatrix} \alpha & \beta & \cdots & 0 \\ \beta & \alpha & \cdots & 0 \\ \vdots & \vdots & \cdots & \vdots \\ 0 & 0 & \cdots & \alpha \end{pmatrix} \begin{pmatrix} X_1 \\ X_2 \\ \vdots \\ X_N \end{pmatrix} = E \begin{pmatrix} X_1 \\ X_2 \\ \vdots \\ X_N \end{pmatrix}$$

$$\alpha X_n + \beta(X_{n-1} + X_{n+1}) = EX_n$$

Let $X_n = X_0 e^{ikna} \quad \Rightarrow X_0 e^{ikna}\left(\alpha + 2\beta\cos(ka)\right) = X_0 e^{ikna} E_k$

$$E_k = \alpha + 2\beta\cos(ka)$$

Extension of approximate "linear combination of atomic orbital" idea to larger systems – simple cubic lattice



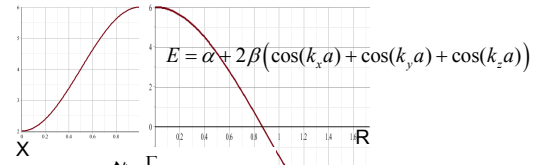
Nearest neighbors:

$\pm a\hat{\mathbf{x}}, \quad \pm a\hat{\mathbf{y}}, \quad \pm a\hat{\mathbf{z}}$

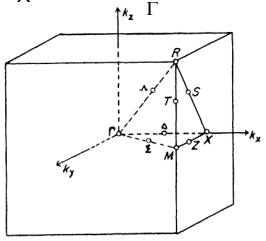
$$\Psi_{n\mathbf{k}} = e^{i\mathbf{k}\cdot\mathbf{R}_n} u(\mathbf{r})$$

Model Hamiltonian: $H_{nn'} = \begin{cases} \alpha & n' = n \\ \beta & n' \text{ and } n \text{ are nearest neighbors} \\ 0 & \text{otherwise} \end{cases}$

$$E = \alpha + 2\beta\left(\cos(k_x a) + \cos(k_y a) + \cos(k_z a)\right)$$



$$E = \alpha + 2\beta\left(\cos(k_x a) + \cos(k_y a) + \cos(k_z a)\right)$$



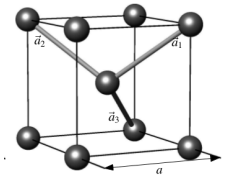
Special points in Brillouin zone:

$X \quad \left(\frac{\pi}{a}, 0, 0\right)$

$\Gamma \quad (0,0,0)$

$R \quad \left(\frac{\pi}{a}, \frac{\pi}{a}, \frac{\pi}{a}\right)$

Extension of approximate "linear combination of atomic orbital" idea to larger systems – body centered cubic lattice

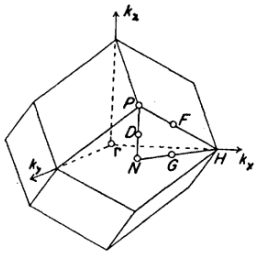


Nearest neighbors:

$$\pm\frac{a}{2}\hat{\mathbf{x}} \pm \frac{a}{2}\hat{\mathbf{y}} \pm \frac{a}{2}\hat{\mathbf{z}}$$

Model Hamiltonian: $H_{nn'} = \begin{cases} \alpha & n' = n \\ \beta & n' \text{ and } n \text{ are nearest neighbors} \\ 0 & \text{otherwise} \end{cases}$

$$E = \alpha + 8\beta\left(\cos\left(\frac{k_x a}{2}\right)\cos\left(\frac{k_y a}{2}\right)\cos\left(\frac{k_z a}{2}\right)\right)$$

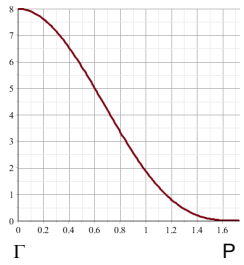


Special points in Brillouin zone:

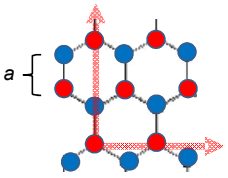
H $\left(\frac{2\pi}{a},0,0\right)$

Γ $(0,0,0)$

P $\left(\frac{\pi}{a},\frac{\pi}{a},\frac{\pi}{a}\right)$



Honeycomb lattice (graphene sheet)



red atoms:

$$\mathbf{r}_i = \boldsymbol{\tau}_{\text{red}} + n_{1i}\mathbf{a}_1 + n_{2i}\mathbf{a}_2$$

blue atoms:

$$\mathbf{r}_i = \boldsymbol{\tau}_{\text{blue}} + n_{1i}\mathbf{a}_1 + n_{2i}\mathbf{a}_2$$

$$\mathbf{a}_1 = \sqrt{3}a\hat{\mathbf{x}} \qquad \mathbf{a}_2 = \sqrt{3}a\left(\frac{1}{2}\hat{\mathbf{x}} + \frac{\sqrt{3}}{2}\hat{\mathbf{y}}\right)$$

$$\boldsymbol{\tau}_{\text{red}} = 0 \qquad \boldsymbol{\tau}_{\text{blue}} = a\hat{\mathbf{y}}$$

Tight binding electronic structure of graphite -- continued

$$H = \begin{pmatrix} H_{rr} & H_{rb} \\ H_{br} & H_{bb} \end{pmatrix}$$

$$H_{rr} = H_{bb} = E_0$$

$$H_{rb} = E_1\left(e^{ik_y a/\sqrt{3}} + 2e^{-ik_y a/(2\sqrt{3})}\cos(k_x a/2)\right)$$

$$E_{\pm} = E_0 \pm E_1\sqrt{1 + 4\cos^2(k_x a/2) + \cos\left(\sqrt{3}k_y a/2\right)\cos(k_x a/2)}$$